

AD-A137 216

VIBRATIONAL SPECTROSCOPY OF ACETYLENE DECOMPOSITION ON  
PALLADIUM (111) AND (100) SURFACES(U) INDIANA UNIV AT  
BLOOMINGTON DEPT OF PHYSICS L L KESMODEL ET AL.

1/1

UNCLASSIFIED

16 JAN 84 TR-8 N00014-80-C-0147

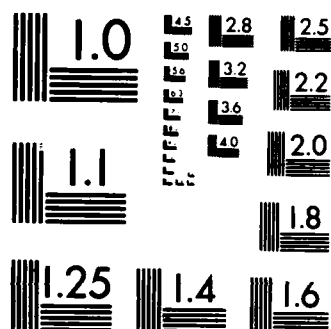
F/G 7/4

NL

END

FILMED

DTIC

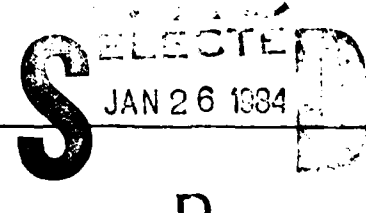


MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

12

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 8	2. GOVT ACCESSION NO. AD-A137216	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Vibrational Spectroscopy of Acetylene Decomposition on Palladium (111) and (100) Surfaces		5. TYPE OF REPORT & PERIOD COVERED Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) L.L. Kesmodel, G.D. Waddill, and J.A. Gates		8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0147
9. PERFORMING ORGANIZATION NAME AND ADDRESS Indiana University Foundation Department of Physics Indiana University, Bloomington, IN 47405		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physics Program Office Arlington, VA 22217		12. REPORT DATE January 16, 1984
		13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  <div style="text-align: right;">  <p>SELECTED JAN 26 1984 D</p> </div>		
18. SUPPLEMENTARY NOTES  To be published in <u>Surface Science</u> (1984)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Acetylene; benzene; palladium (100) and (111) surfaces; vibrational spectroscopy; electron energy loss spectroscopy; chemisorption and catalysis; thermal decomposition; CCH formation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Vibrational spectra for thermal decomposition of acetylene ( $C_2H_2$ ) on (111) and (100) surfaces of palladium obtained with high-resolution electron energy loss spectroscopy (EELS) are described. Of particular interest is the formation of CCH species on both surfaces, which are identified spectroscopically in this context for the first time. On Pd(100) CCH forms with thermal processing of chemisorbed acetylene to ~400K but on Pd(111) is co-adsorbed with a $\equiv C-CH_3$ species following 300K $C_2H_2$ adsorption. With		

DD FORM 1473  
1 JAN 73

EDITION OF 1 NOV 68 IS OBSOLETE

S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

84 01 26 015

AD A 137216

DTIC FILE COPY

further annealing to 450K CCH is the dominant species on both surfaces. The EELS spectra indicate that both carbon atoms are involved in the CCH interaction with the surface as implied by a C-C bond order between 1 and 2. In view of recent reports of acetylene trimerization to benzene ( $C_6H_6$ ) on Pd surfaces the EELS spectra of  $C_6H_6$  and isotopic mixtures were also analyzed but no evidence for this reaction was found.

OFFICE OF NAVAL RESEARCH

Contract N00014-80-C-0147

Technical Report No. 8

VIBRATIONAL SPECTROSCOPY OF ACETYLENE DECOMPOSITION  
ON PALLADIUM (111) AND (100) SURFACES

by

L.L. Kesmodel, G.D. Waddill, and J.A. Gates  
Department of Physics  
Indiana University  
Bloomington, Indiana 47405

16 January 1984

Reproduction in whole or in part is permitted for any  
purpose of the United States Government.

Approved for Public Release; Distribution Unlimited

Published in Surface Sciences (1984), in press.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A/1	



Vibrational Spectroscopy of Acetylene Decomposition  
on Palladium (111) and (100) Surfaces

by

L.L. Kesmodel\*, G.D. Waddill, and J.A. Gates

Department of Physics

Indiana University

Bloomington, Indiana 47405, U.S.A.

Submitted to Surface Science

\*To whom correspondence should be addressed.

Abstract

triple bond  
approx.

Vibrational spectra for thermal decomposition of acetylene ( $C_2H_2$ ) on (111) and (100) surfaces of palladium obtained with high-resolution electron energy loss spectroscopy (EELS) are described. Of particular interest is the formation of CCH species on both surfaces, which are identified spectroscopically in this context for the first time. On Pd(100) CCH forms with thermal processing of chemisorbed acetylene to 400K but on Pd(111) is co-adsorbed with a  $C-CH_3$  species following 300K  $C_2H_2$  adsorption. With further annealing to 450K CCH is the dominant species on both surfaces. The EELS spectra indicate that both carbon atoms are involved in the CCH interaction with the surface as implied by a C-C bond order between 1 and 2. In view of recent reports of acetylene trimerization to benzene ( $C_6H_6$ ) on Pd surfaces the EELS spectra of  $C_6H_6$  and isotopic mixtures were also analyzed but no evidence for this reaction was found.

## 1. Introduction

Recent spectroscopic studies of acetylene ( $C_2H_2$ ) chemistry on palladium surfaces by several research groups [1-5] have raised many questions concerning the thermal evolution of this species. In high-resolution electron energy loss (EELS) studies on Pd(111) the formation of  $CCH_2$ ,  $CCH_3$ , and CH species were detected as thermal evolution products of initially chemisorbed  $C_2H_2$  in the temperature range 150-500K [1,2]. However, in subsequent studies with thermal desorption spectroscopy (TDS) [3-5] and ultraviolet photoemission spectroscopy (UPS) [3,4] the formation of benzene ( $C_6H_6$ ) has been emphasized. Ethylene formation was also reported [4,5]. Several questions remain concerning possible  $C_6H_6$  formation: UPS evidence [3,4] for this species is not definitive, and aspects of the TDS results are inconsistent. For example, in the study by Sesselmann et al. [3]  $C_6H_6$  was reportedly formed only under low temperature and high exposure ( $> 100L$ ) conditions whereas Tysoe et al. [4] and Gentle and Muetterties [5] detected reactively-formed  $C_6H_6$  at both low (230K) and high (500K) temperatures. We note that the studies in Refs. 1-4 were restricted to the (111) surface whereas (111), (100), and (110) surfaces were considered in Ref. 5.

The central issue addressed in the present work concerns the nature of acetylene-derived species present on both Pd(111) and Pd(100) surfaces in the temperature range 300-500K. In this regard the work expands on our earlier EELS studies on Pd(111) [2] and focuses on the question of  $C_6H_6$  formation. Detailed EELS



analysis of  $C_2H_2$ ,  $C_6H_6$  and their deuterated counterparts were carried out, including various isotope mixing experiments. Although a 450K acetylene-derived surface species observed on both Pd(111) and Pd(100) exhibits vibrational features similar to benzene we find that this species is, in fact, CCH. On Pd(100) the CCH species is formed near 400K from  $\sim sp^3$  hybridized acetylene. On Pd(111) both CCH and ethylidyne ( $\equiv C-CH_3$ ) [2] are formed upon adsorption of  $C_2H_2$  at 300K, the ethylidyne species decomposing by 450K. The Pd(100) vibrational data suggests that the CCH stereochemistry involves bonding of both carbon atoms to the surface with a bond order between 1 and 2.

Our lack of EELS vibrational evidence for benzene formation does not directly conflict with the recent studies [3-5] but rather suggests that benzene may be (i) formed in relatively small amounts on the surface or (ii) largely formed in a process leading to rapid desorption.

## 2. Experimental Procedures

The high-resolution electron energy loss measurements were carried out with two 127° cylindrical deflection electron spectrometers at Indiana University. The Pd(111) experiments were performed with a single-pass instrument [6] which is housed in an ion-pumped ultrahigh vacuum system (base pressure  $\sim 1 \times 10^{-10}$  Torr), also equipped for ion-sputtering, low-energy electron diffraction and Auger spectroscopy. This instrument was operated at 10 meV ( $80 \text{ cm}^{-1}$ ) system resolution at typical elastic beam signal levels of  $0.3\text{--}1.0 \times 10^5$  cps for hydrocarbon adsorption. The Pd(100) experiments employed a new double-pass spectrometer which achieves high signal levels at 2.5–10 meV system resolution [7]. This instrument is incorporated in a diffusion/sublimation-pumped system (base pressure  $\sim 5 \times 10^{-11}$  Torr) equipped for ion-sputtering and mass spectrometry. Due to the generally low intensity of the hydrocarbon modes the spectrometer was operated at 8–9 meV ( $64\text{--}72 \text{ cm}^{-1}$ ) system resolution providing specular elastic beam count rates of  $\sim 2 \times 10^6$  cps at beam energies of 4–6 eV. The high sensitivity afforded under these conditions proved valuable for detection of weak losses and facilitated off-specular measurements.

Sample preparation and cleaning for the EELS experiments has been described elsewhere [2]. High purity  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{D}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{D}_6$ ,  $\text{H}_2$ , and  $\text{D}_2$  gases were used and were examined with a mass spectrometer for impurities. Hydrocarbon exposures quoted in Langmuirs ( $1\text{L} = 10^{-6} \text{ Torr-s}$ ) were corrected for reported

ion-gauge sensitivity [8].

### 3. Results

Extensive high-resolution EELS spectra for  $C_2H_2$ ,  $C_2D_2$ ,  $C_6H_6$ , and  $C_6D_6$  on Pd(111) and Pd(100) have been obtained under various temperature and coverage conditions; isotope mixing experiments ( $C_2H_2 + C_2D_2$ ,  $C_6H_6 + D_2$ , etc.) have been performed as well. In this section the salient results of this study are discussed with emphasis on (i) the possible detection of  $C_2H_2$  trimerization to  $C_6H_6$  and (ii) the nature of acetylene decomposition product(s) in the temperature range 300-500K.

#### 3.1. Pd(100) vibrational spectra

The EELS spectrum for 300K adsorption of  $C_2H_2$  on Pd(100) is shown in Fig. 1a. As discussed elsewhere [9] this spectrum is due to acetylene in a near  $sp^3$  hybridization state as evidenced by  $\nu_{CC} = 1210 \text{ cm}^{-1}$  and  $\nu_{CH} = 2920 \text{ cm}^{-1}$ . This spectrum transforms upon warming to 450K (Fig. 1b) to one resembling those reported for CH species on (111) surfaces of Ni, Pd, Pt, and Rh [10]; characteristic is the strong CH bending loss at  $750 \text{ cm}^{-1}$  and the CH stretch at  $3000 \text{ cm}^{-1}$ . However, a broad band ca.  $1340 \text{ cm}^{-1}$  is also found which does not appreciably shift with deuteration and is, therefore, assigned to a CC stretching mode. Importantly, we find that the  $750 \text{ cm}^{-1}$ ,  $1340 \text{ cm}^{-1}$ , and  $3000 \text{ cm}^{-1}$  loss intensities decay at the same rate (within experimental error of 10%) upon thermal processing from 475K to 650K. This is strong evidence that a single surface species is responsible for these modes. A likely interpretation of Fig. 1b is thus in terms of a

multiply-bonded CCH species.

Figure 1c indicates that  $C_6H_6$  formation might also provide an explanation of the 450K acetylene-derived species. Benzene adsorbed at 300K is fairly stable until ~500K with an EELS spectrum characterized by a very intense loss at  $730\text{ cm}^{-1}$  with much weaker losses at 1130, 1440, and  $3020\text{ cm}^{-1}$ . Quite similar spectra have been reported for  $C_6H_6$  adsorption on Ni(111) [11,12], Ni(100) [12], Pt(111) [11], and Rh(111) [13] and consistently interpreted in terms of predominant  $\pi$ -bonding with the benzene ring parallel to the surface. The exceptionally strong loss at  $730\text{ cm}^{-1}$  is assigned to the  $\nu_4$  out-of-plane CH bending mode of  $A_{2u}$  symmetry and  $673\text{ cm}^{-1}$  frequency in the gas phase [14,15]. This mode has strong infrared activity in the gas phase and will be dipole active on the surface for parallel adsorption. The resemblance of major features of Figs. 1b,c leaves  $C_6H_6$  formation a possibility we discuss further below.

### 3.2. Pd(111) vibrational spectra

EELS vibrational spectra for 150K  $C_2H_2$  adsorption and thermal evolution were reported earlier [2]. It was found that  $C_2H_2$  chemisorbed at 150K in an  $sp^{2.5}$  hybridization state (Fig. 2a,  $\nu_{CC} = 1400\text{ cm}^{-1}$ ,  $\nu_{CH} = 2990\text{ cm}^{-1}$ ) and underwent hydrogenation to ethylidyne ( $\equiv C-CH_3$ ) near 300K via a probable vinylidene ( $=C=CH_2$ ) intermediate. Here we consider room temperature  $C_2H_2$  adsorption at relatively low (1.5L) and higher (12L) exposures. Under these conditions a mixture of ethylidyne and CCH species form as shown in Fig. 2b,c. Ethylidyne has been

characterized [2] in terms of strong modes near  $1330\text{ cm}^{-1}$  (methyl deform.) and  $1100\text{ cm}^{-1}$  (CC stretch). These modes are present for 300K adsorption along with the strong CH bending vibration indicative of CCH (or possibly  $\text{C}_6\text{H}_6$ ). Upon warming to 500K decomposition of ethylidyne has occurred but the  $750\text{ cm}^{-1}$  loss remains (Fig. 2d). As noted for the (100) surface this spectrum is quite similar to the EELS spectrum for associatively adsorbed  $\text{C}_6\text{H}_6$  (Fig. 2e). Signal-to-noise levels in the Pd(111) study were not sufficient to permit conclusive identification of  $\text{C}_6\text{H}_6$  loss features in the  $1000\text{--}1500\text{ cm}^{-1}$  region for Fig. 2d,e. However, comparison of the Pd(100) and (111) spectra strongly suggests that the same acetylene-derived species is present on both surfaces at 450K. Finally, we note a 300K exposure-dependent ratio of this product and ethylidyne evident in Fig. 2b,c. This aspect will be discussed in a subsequent paper in connection with hydrogen thermal desorption results.

### 3.3. Off-specular analysis

In order to further explore possible detection of  $\text{C}_6\text{H}_6$  formation selected off-specular analyses comparing  $\text{C}_6\text{H}_6$  and the 475K acetylene-derived species were undertaken on Pd(100). As shown in Fig. 3b,c marked differences between  $\text{C}_6\text{H}_6$  and the  $\text{C}_2\text{H}_2$ -derived species occur in the  $1000\text{--}1600\text{ cm}^{-1}$  region. The  $\nu_{\text{CH}}$  loss is also much stronger for the latter species. As shown in Fig. 3a the broad  $1360\text{ cm}^{-1}$  band is hardly shifted upon deuteration.

These spectra indicate that the species is not benzene but

rather CCH. In Fig. 3a the presence of a small amount of CCH in the CCD spectrum is evident from weak features near  $750\text{ cm}^{-1}$  (shoulder) and  $3000\text{ cm}^{-1}$ . Other features of note are the presence of shoulders at  $850$  ( $640$ )  $\text{cm}^{-1}$  in the CCH (CCD) spectra. These weaker modes may be due to the other CH bending mode (parallel to the surface plane) or to CCH species in another surface bonding configuration. The latter interpretation is consistent with the broad nature of the  $\nu_{\text{CC}}$  band centered at  $1360\text{ cm}^{-1}$ . We rule out  $\text{CCH}_2$  or  $\text{CH}_2$  species due to the absence of characteristic scissor vibrations ( $\text{ca. } 1400\text{ cm}^{-1}$ ) and on the basis of isotope mixing experiments discussed below.

#### 3.4. Isotope mixing experiments

If the acetylene-derived species formed at 450K is  $\text{C}_6\text{H}_6$  it is clear that mixtures of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$  will give rise to  $\text{C}_6\text{H}_x\text{D}_{6-x}$  molecules with even  $x$ ; the other isotopes will occur if H-D exchange occurs. Furthermore, by scaling to known gas phase frequencies for the strong  $\nu_4$  bending mode [15] reasonable predictions for the surface isotopes can be made. This mode should be dipole active in each case for parallel-bonded benzene. The various bands ( $\nu_4$ ) are found to occur in separated groupings [15] and the predicted surface frequencies are, for example:  $\text{C}_6\text{D}_6$  ( $545\text{ cm}^{-1}$ ); sym- $\text{C}_6\text{H}_3\text{D}_3$  ( $588\text{ cm}^{-1}$ ); para- $\text{C}_6\text{H}_4\text{D}_2$  ( $658\text{ cm}^{-1}$ );  $\text{C}_6\text{H}_6$  ( $740\text{ cm}^{-1}$ ). Benzene mixtures should, therefore, be characterized by a very broad band between  $545\text{--}740\text{ cm}^{-1}$ . Such a band was consistently produced by mixing  $\text{C}_6\text{H}_6$  with  $\text{D}_2$  at 150K on Pd(111) and warming to 450K. Figure 4 provides clear evidence

for statistically probable  $C_6H_3D_3$  or  $C_6H_2D_4$  isotopes whereas  $C_6D_6$  is largely absent as expected. Another loss appearing as a shoulder near  $825\text{ cm}^{-1}$  is quite probably due to another strong mode for one of the isotopes [16]. These results (and similar ones for  $C_6D_6 + H_2$ ) are qualitatively different than predictions for the CCH model which would, of course, simply give rise to the same two bands when  $C_2H_2$  and  $C_2D_2$  are mixed.

Isotope mixing of  $C_2H_2$  and  $C_2D_2$  are illustrated in Fig. 5 for Pd(100). Panel (a) shows the unreacted mixture at 300K which gives rise to two strong modes at  $545\text{ cm}^{-1}$  and  $\sim 770\text{ cm}^{-1}$  upon warming to 450K. Analogous results were obtained on the (111) surface. This result clearly favors the CCH model and rules out  $C_6H_6$  formation. In the benzene model, for example, the  $770\text{ cm}^{-1}$  mode associated with pure  $C_6H_6$  would have very low statistical weight for the 1:2 mixture, contrary to the EELS spectra (Fig. 5). Furthermore, we find that calibration to relative loss intensities for the separate  $C_2H_2$  and  $C_2D_2$  heating experiments allows fairly accurate prediction (5-20% error) of relative intensities of the two loss peaks for various isotope mixing ratios. This result again strongly supports the CCH model but cannot be reconciled with the benzene model or other polymerization products.

#### 4. Conclusions

The high-resolution EEL<sup>-</sup> data discussed in Sec. 3 provides rather clear spectral evidence for CCH formation from C<sub>2</sub>H<sub>2</sub> on both (111) and (100) palladium surfaces. Although this species was interpreted as CH in earlier work on Pd(111) [2] the present investigation strongly favors the CCH model since the band attributable to  $\nu_{CC}$  is consistently found on the (100) surface. Furthermore, an appealing aspect of room-temperature CCH formation on Pd(111) is the release of hydrogen necessary to also form the  $\equiv C-CH_3$  species from acetylene. This is the first clear evidence for such a species on (100) and (111) surfaces of Pd or related metals although a CCH species was proposed on Ni(110) in UPS studies [17]. In this regard it may be important to reconsider the earlier assignments made to CH species on Ni, Pt, and Rh [10] in terms of CCH formation due to the close resemblance of the various spectra.

Evidently CCH stereochemistry on palladium involves bonding of both carbon atoms to the metal surface leading to a C-C bond order between 1 and 2 judging from the present EELS results. We postulate that a likely bonding geometry involves the C-C axis parallel or slightly skewed to the surface, consistent with a strong CH bending loss and a weak loss due to the CC stretch. These general features would not be sensitive to structural details on the (100) and (111) surfaces.

We also note the high stability of the CCH species. Thermal processing measurements on Pd(100) indicate that decomposition



begins only after ~550K and ~30% of the original species remains at 650K. In this regard, ab initio calculations on CCH bonding geometry and relative stability compared to  $C_2H_2$ , CH, etc., would be of considerable interest.

#### Acknowledgments

We are grateful to Dr. J.E. Demuth for his interest in this work and for numerous stimulating discussions. We thank Drs. G. Ertl, R.M. Lambert, and E.L. Muetterties for kindly providing preprints of their work prior to publication. We also thank Mr. Hye Keun O for his able technical assistance. This work was supported by the Office of Naval Research.

References

- [1] J.A. Gates and L.L. Kesmodel, J. Chem. Phys. 76 (1982) 4281.
- [2] J.A. Gates and L.L. Kesmodel, Surface Sci. 124 (1983) 68.
- [3] W. Sessellmann, B. Woratschek, G. Ertl, J. Kuppers, and H. Haberland, Surface Sci., to be published.
- [4] W.T. Tysoe, G.L. Nyberg, and R.M. Lambert, Surface Sci., to be published.
- [5] T.M. Gentle and E.L. Muetterties, J. Phys. Chem. 87 (1983) 2469.
- [6] L.L. Kesmodel, J.A. Gates, and Y.W. Chung, Phys. Rev. B23 (1981) 489.
- [7] L.L. Kesmodel, J. Vacuum Sci. Technol., in press.
- [8] Varian ionization gauge sensitivity factors: acetylene, 2.0; benzene, 6.0.
- [9] L.L. Kesmodel, J. Chem. Phys., to be published.
- [10] A tabulation of data and further references are given in Ref. 2.
- [11] S. Lehwald, H. Ibach, and J.E. Demuth, Surface Sci. 78 (1978) 577.
- [12] J. Bertolini and J. Rousseau, Surface Sci. 89 (1979) 467.
- [13] B.E. Koel and G.A. Somorjai, J. Electron Spect. Rel. Phenom. 29 (1983) 287.
- [14] T. Shimanouchi, Tables of Molecular Vibrational Frequencies Consolidated Vol. I, NSRDS-NBS 39, 1972.
- [15] L.M. Sverdlov, M.A. Kovner, and E.P. Krainov, Vibrational Spectra of Polyatomic Molecules (Wiley, New York, 1974)

p. 324.

[16] We find a mode of medium intensity ca.  $830\text{ cm}^{-1}$  for  $\text{C}_6\text{D}_6$  on Pd(111); a similar mode was reported on Rh(111) [13].

[17] J.E. Demuth, Surface Sci. 93 (1980) 127.

Figure Captions

Fig. 1: High-resolution EELS spectra for hydrocarbon adsorption on Pd(100).

(a) 10L  $C_2H_2$  exposure at 300K

(b) Thermal processing of (a) to 450K

(c) 2L  $C_6H_6$  exposure at 300K

Scale changes refer to the elastic beam for each panel in this and subsequent figures.

Fig. 2: High-resolution EELS spectra for hydrocarbon adsorption on Pd(111).

acetylene: (a) 3 L exposure at 150K,

(b) 1.5 L exposure at 300K,

(c) 12 L exposure at 300K,

(d) Thermal processing of (c) to 500K

benzene: (e) 1 L exposure at 300K, warmed to 450K.

Fig. 3: Comparison of high-resolution EELS spectra for the 475K acetylene-derived surface phase and benzene for off-specular scattering on Pd(100).

Fig. 4: High-resolution EELS spectra due to mixing of  $C_6H_6$  and  $D_2$  on Pd(111). Lines labeled A-D show the predicted positions for various benzene isotopes due to the  $\nu_4$  modes (see text). Positions of sym- $C_6H_3D_3$ , para- $C_6H_4D_2$ , and para- $C_6H_2D_4$  are shown. The additional ortho-, meta- $C_6H_4D_2$ , 1,2,3- $C_6H_3D_3$ , etc., isotopes

are slightly shifted from the respective groupings shown [15]. Information on the  $C_6HD_5$  isotope was not found for this mode.

Fig. 5: High-resolution EELS spectra due to isotope mixing of  $C_2H_2$  and  $C_2D_2$  on Pd(100).

(a) 300K spectrum due to co-adsorbed

$C_2H_2$  and  $C_2D_2$ .

(b) Thermal processing of (a) to 450K leads

to CCH, CCD spectrum. Dashed lines

indicate predicted isotope vibrational

losses in the event of benzene

formation (cf. Fig. 4).

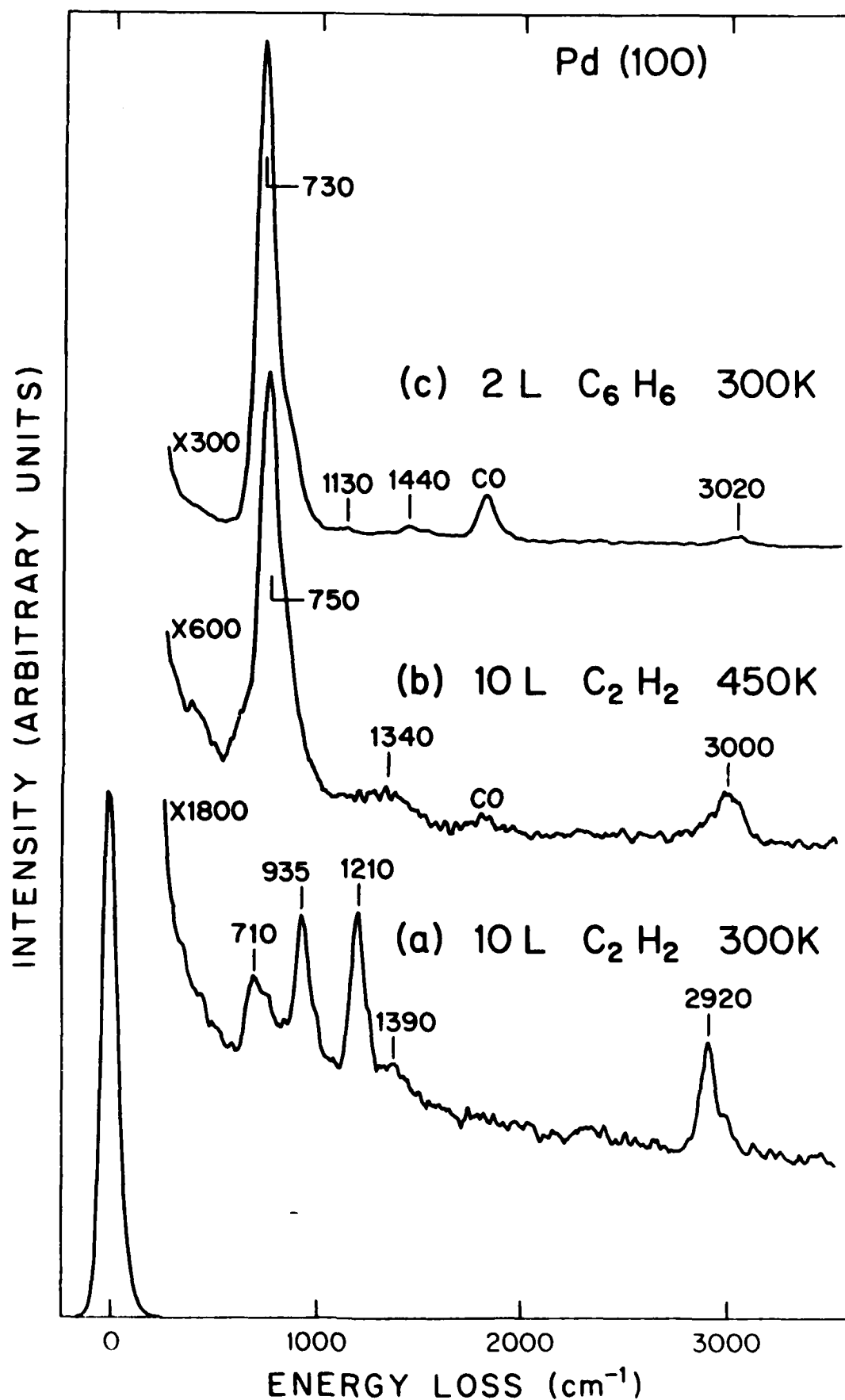


Fig. 1



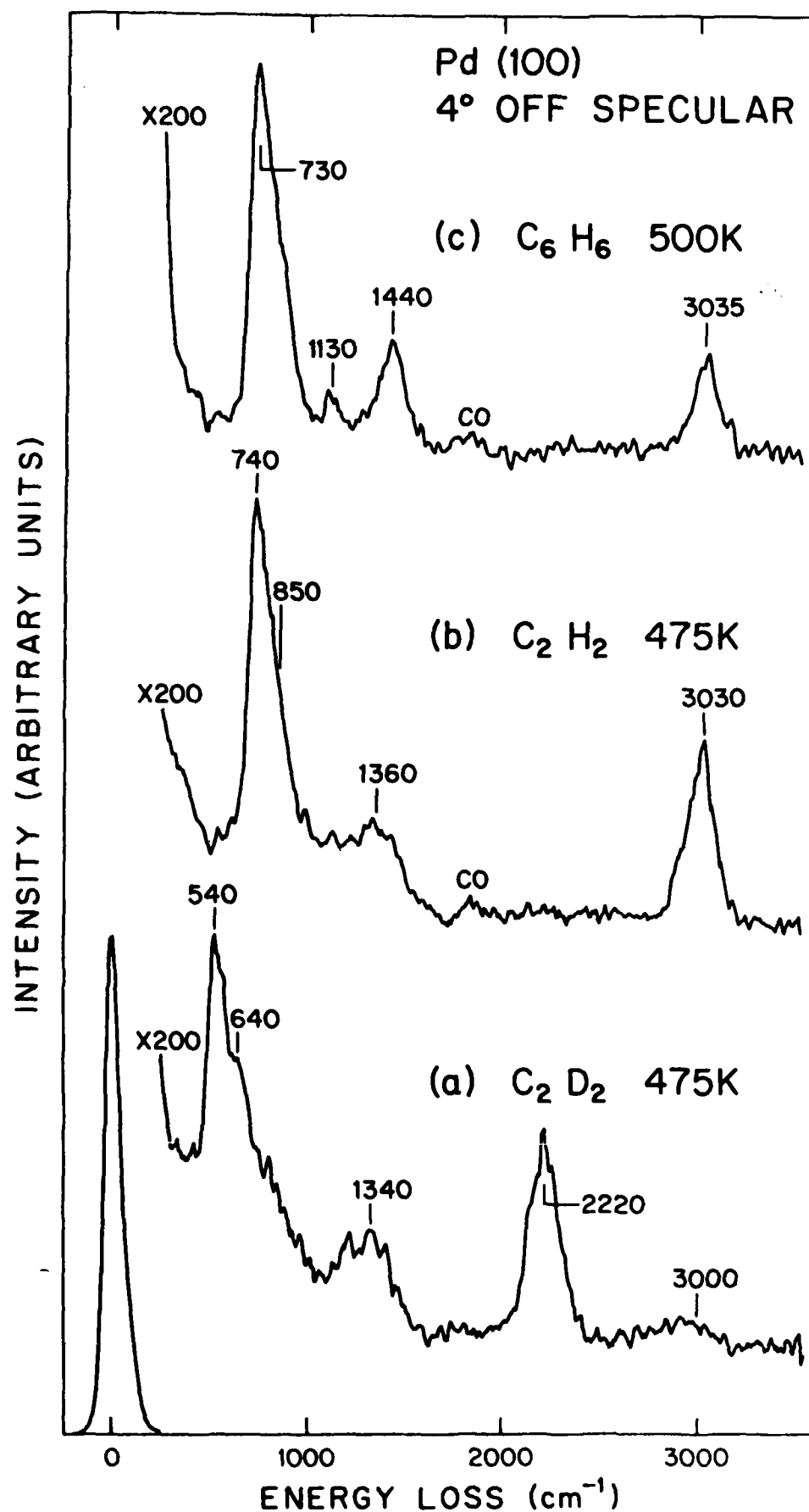


Fig. 3



INTENSITY (ARBITRARY UNITS)

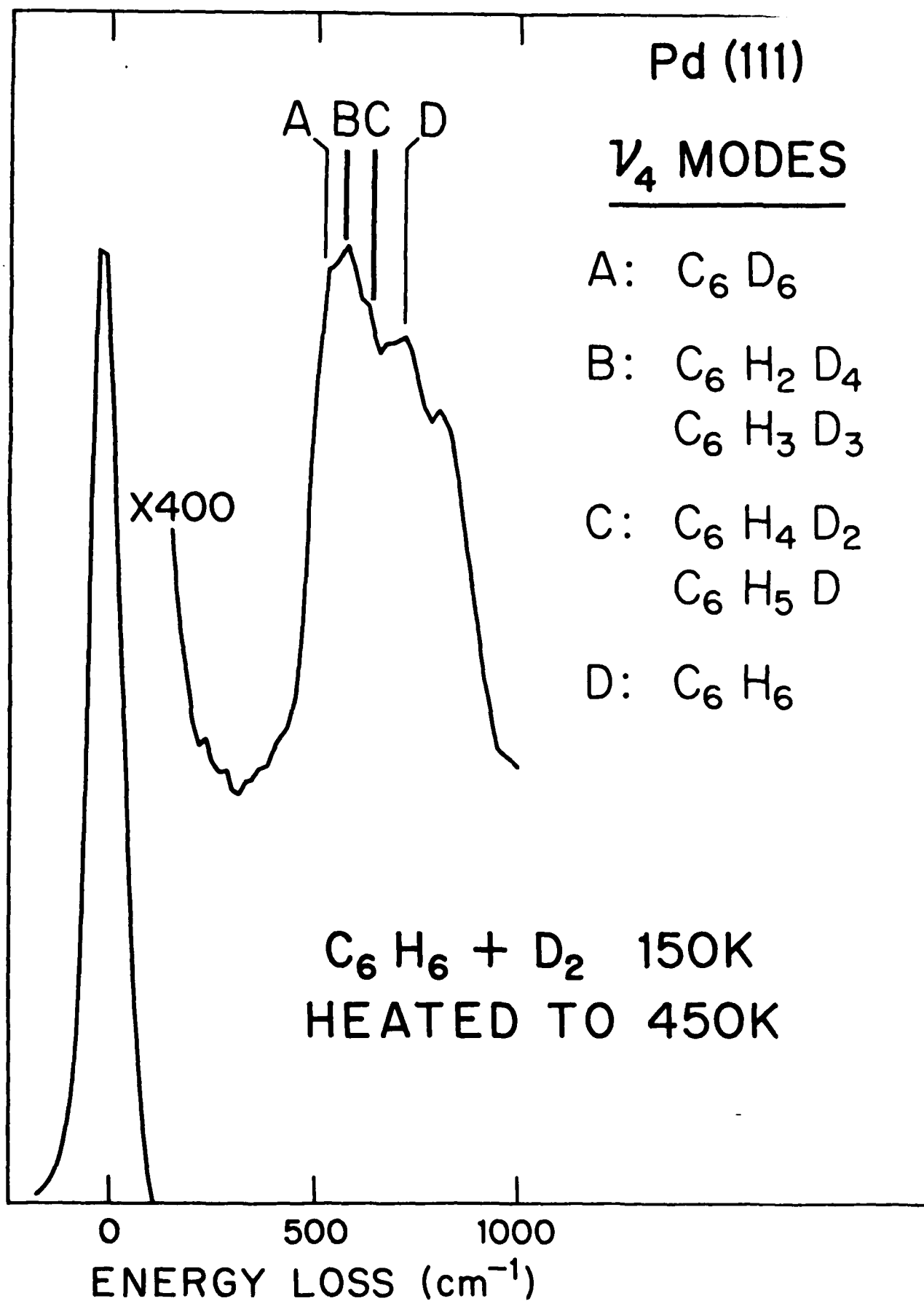


Fig. 4

INTENSITY (ARBITRARY UNITS)

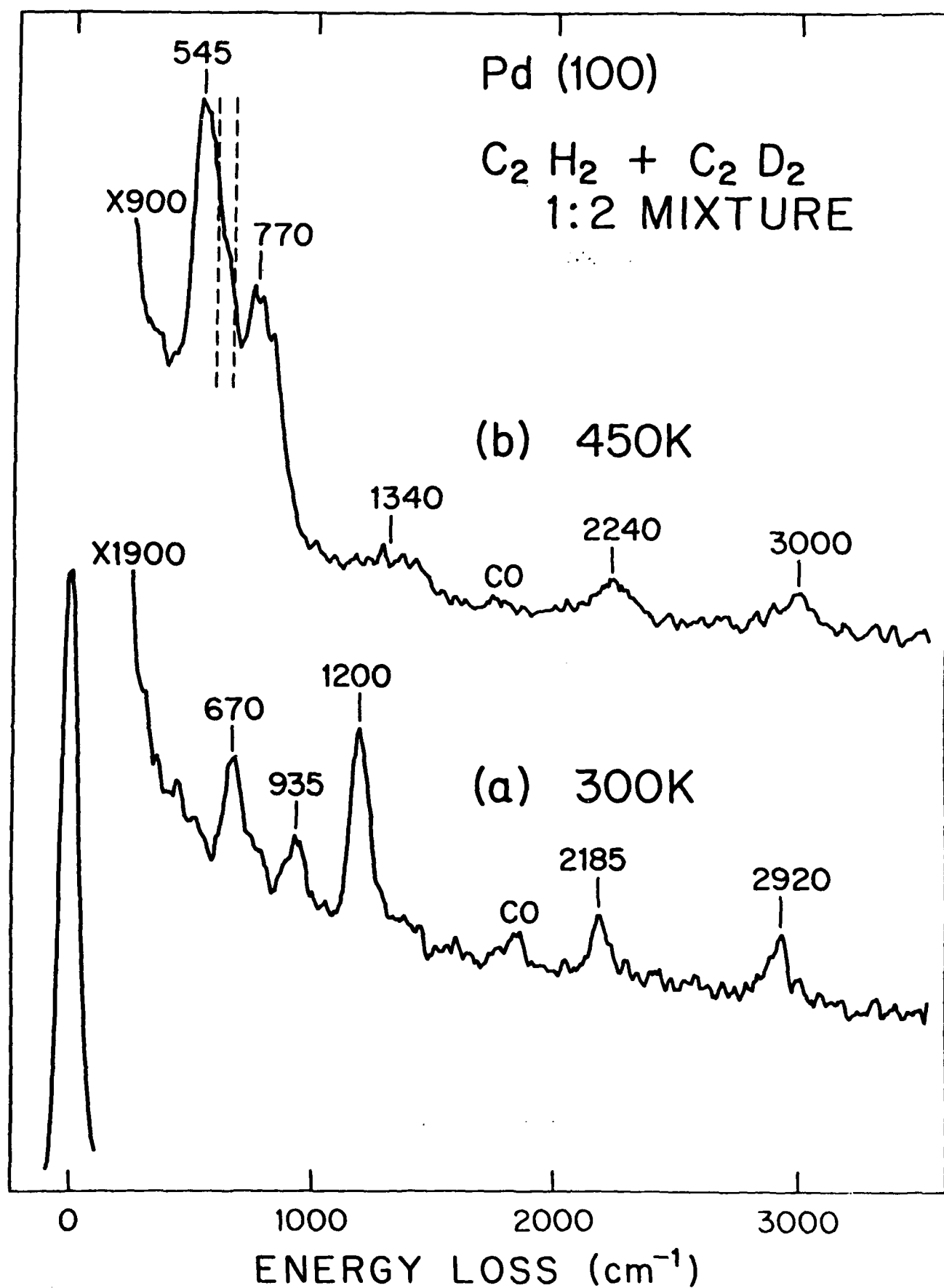


Fig. 5

**FILMED**

02-84